6,6-Dimethylfulvene is thus seen to be an indicator substrate. The first of its kind, it readily differentiates electrophilic from nucleophilic carbene additions. Moreover, the observed regiochemistries of addition are nicely compatible with theoretical expectations. The overall result again demonstrates the power of combined experimental and theoretical analysis of carbenic reactivity.[30] We are continuing our studies of indicator substrates.

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(29) Additions of similarly stabilized carbenes (CF_2, CFOH, and $C(OH)_2$) to ethylene are calculated to have larger overlap at the transition state for CXY^{HO}/alkene^{LU} interaction than for CXY^{LU}/alkene^{HO} interaction.[6] These findings parallel our interpretation of the CH_3OCCl/**1** reaction. A perceptive referee has pointed out that because both interaction terms contribute to the endocyclic addition of CH_3OCCl, FMO theory might actually incorrectly predict this to be the favored mode of reaction, rather than the (observed) exocyclic addition, to which only the nucleophilic interaction can contribute. An extensive analysis of the reaction surface would be needed in order to locate the transition states and accurately evaluate the FMO interaction terms. This is calculationally impossible for systems as complicated as **1** and CH_3OCCl and would probably also stretch the applicability and accuracy of this approach beyond its limits. The transition state obtained in ref 6 for the model ambiphile HOCF adding to ethylene shows strong carbene interaction with one carbon of the ethylene. Analogously, the very large LUMO coefficient of C_6 of **1** may be the dominant factor in establishing large overlap at C_6 and thus controlling the regioselectivity of the CH_3OCCl addition to **1**.

(30) For a prior example, see: Moss, R. A.; Vezza, M.; Guo, W.; Munjal, R. C.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* 1979, *101*, 5088.

On the Heat Capacities of Activation for Displacements at Primary and Secondary Carbon Centers in Water

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The heat capacities of activation ($\Delta C_p^{\ddagger}$) related to solvolytic displacements in water

$$RX + 2H_2O \rightarrow ROH + H_3O^+ + X^- \qquad (1)$$

are invariably negative.[1] An analogy based on other ionogenic reactions in water, e.g., Brönsted acid-base reactions, provides a qualitative explanation for the above observation. Such a model leads to the reasonable conclusion that transition states related to the reactions summarized by eq 1 have considerable ionic character.

Some time ago Albery and Robinson[2] virtually discarded this model for the case RX = *tert*-butyl chloride. These authors postulated that the non-Arrhenius temperature dependence of the solvolytic rates arises as a consequence of an intermediate in the displacement reaction. Such a postulate is not uncongenial in the case of the tertiary center, but its wider application to primary and secondary substrates was considered to be incorrect.[3]

Table I. Rate and Temperature Data for the Hydrolysis of Ethyl Bromide

T, °C	$k \times 10^4$,[a] s^{-1}	$\Delta k \times 10^7$ [b]	k(I) × 10^4, s^{-1}	k(II) × 10^4, s^{-1}	k(III) × 10^4, s^{-1}
90.000	6.8313	4.04	6.8322	6.8314	6.8298
85.016	4.3503	5.13	4.3501	4.3496	4.3612
80.008	2.7252	4.82	2.7224	2.7221	2.7310
80.001	2.7230	4.08	2.7206	2.7203	2.7291
74.840	1.6493	2.08	1.6496	1.6494	1.6527
69.986	1.0117	0.58	1.0122	1.0121	1.0122
65.067	0.60518	0.56	0.60488	0.60480	0.60418
62.583	0.46255	0.46	0.46246	0.46240	0.46203
57.600	0.26463	0.26	0.26470	0.26467	0.26545

[a] The mean of 3-5 determinations, Δk is the standard deviation. [b] The Δk values were used as weighing factors in the Wentworth Regression; ΔT was fixed at 0.001 K for all temperatures. The k(I) and k(II) quantities were calculated from the two sets of values of A, B, C, and D appropriate to eq 7, and k(III) was obtained from the values of A, B, and C appropriate to eq 2. The number of significant figures given with respect to k, k(I), k(II), and k(III) is that required to calculate Ω to two significant figures.

Table II. Rate and Temperature Data for the Hydrolysis of *sec*-Propyl Methanesulfonate

T, °C	$k \times 10^4$,[a] s^{-1}	$\Delta k \times 10^7$ [b]	k(I) × 10^4, s^{-1}	k(II) × 10^4, s^{-1}	k(III) × 10^4, s^{-1}
32.520	5.0270	1.41	5.0251	5.0271	5.0249
30.001	3.6858	3.86	3.6889	3.6903	3.6919
30.007	3.6923	4.50	3.6916	3.6931	3.6946
27.502	2.7003	1.50	2.7011	2.7021	2.7044
25.007	1.9640	1.41	1.9640	1.9648	1.9665
22.007	1.3293	1.71	1.3291	1.3296	1.3304
70.005	1.0195	1.29	1.0189	1.1093	1.0195
17.496	0.72678	1.31	0.72570	0.72600	7.2575
14.997	0.51465	0.34	0.51389	0.51410	0.51371
12.495	0.36105	0.17	0.36102	0.36117	0.36084
10.003	0.25195	0.22	0.25199	0.25209	0.25193
7.510	0.17408	0.15	0.17440	0.17447	0.17454
4.997	0.11960	0.14	0.11928	0.11933	0.11961

[a] See footnote *a* of Table I. [b] See footnote *b* of Table I.

A decision between the Albery-Robinson approach and more traditional explanations for non-Arrhenius behavior in displacement reactions is nevertheless difficult, since the magnitude and general behavior of $\Delta C_p^{\ddagger}$ is conditioned largely by the assumptions which underpin its calculation from the rate-temperature (k-T) data. We recently have shown that the temperature dependence of the rates of hydrolysis of ethyl bromide and *sec*-propyl methanesulfonate demonstrate some features which are in agreement with the Albery-Robinson hypothesis.[4] This is of considerable interest, since the primary and secondary reactants in question are traditionally considered to be S_N2 or "borderline" substrates. In the present communication we reexamine the temperature dependence of the k-T data for the two substances mentioned above via the Valentiner equation

$$\ln k = A/T + B \ln T + C \qquad (2)$$

which considers $\Delta C_p^{\ddagger}$ to be real rather than anomalous (spurious[5]). Equation 2 also embodies all the "classical" notions concerning the origins of $\Delta C_p^{\ddagger}$ and tacitly assumes that the barrier to activation relates to a single step. In parallel, we also examine the k-T data for the same substances by using the Albery-Robinson

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(1) R. E. Robertson, *Prog. Phys. Org. Chem.*, **14**, 203 (1977). For an exception, see J. P. Barron, J. G. Winter, and J. M. W. Scott, *Can. J. Chem.*, **53**, 1051 (1975).

(2) J. Albery and B. H. Robinson, *Trans. Faraday Soc.*, **15**, 980 (1969).

(3) R. E. Robertson and J. M. W. Scott, *Can. J. Chem.*, **50**, 169 (1972).

(4) M. J. Blandamer, R. E. Robertson, J. M. W. Scott, and A. Vrielink, *J. Am. Chem. Soc.*, **102**, 2585 (1980).

(5) Both "spurious"[3] and "anomalous"[4] have been used to describe that part of the "heat capacity" which is postulated to derive from mechanistic complexity. See also S. Leung and E. Grunwald, *J. Phys. Chem.*, **74**, 687 (1970).

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Table III. Derived Temperature-Dependence Parameters[a] for the Hydrolysis of Ethyl Bromide and *sec*-Propyl Methanesulfonate

substrate	eq no.	A	B	C	D	$\Omega \times 10^7$	$(\Sigma\Delta k^2)n \times 10^7$
CH_3CH_2Br	2	−20182.8 ±235.1	−23.5054 ±0.727	186.848 ±4.980		5.87	
	7	−18735.5 ±1365.4	48.1172 ±4.3594	−7134.24 ±1280.54	23.4374 ±4.1389	1.71	3.12
	7	−11601.3 ±85.8	24.6798 ±0.2231	7134.24 ±1280.54	−23.4374 ±4.1389	1.88	
$(CH_3)_2CHOSO_3CH_3$	2	−16214.1 ±163.7	−16.012 ±0.577	137.079 ±3.859		2.70	
	7	−15472.7 ±995.9	46.1573 ±3.9808	−4298.91 ±907.11	17.1536 ±3.6285	1.35	1.92
	7	−11173.7 ±89.7	29.0038 ±0.2650	4298.91 ±907.11	−17.1536 ±3.6285	1.71	

[a] The number of significant figures quoted for A, B, C, and D (eq 7) and A, B, and C (eq 2) is that required to reproduce the reported rate constants to a precision which is comparable to the reported errors of the rate data. The number of digits generally exceeds those justified by the errors from the Wentworth algorithm.

treatment. The main point at issue is whether or not the mechanism

$$RX \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{intermediate} \xrightarrow{k_3} \text{products} \quad (3)$$

along with the related steady state expression

$$k_{obsd} = \frac{k_1 k_3}{k_2 + k_3} = \frac{k_1}{1 + \alpha} \quad (4)$$

where $\alpha = k_2/k_3$, will accomodate the k–T data for ethyl bromide and *sec*-propyl methanesulfonate by assuming a simple Arrhenius temperature dependence for the two quantities k_1 and α, such that

$$k_1 = \exp(A/T + B) \quad (5)$$

$$\alpha = \exp(C/T + D) \quad (6)$$

Speculation as to the precise nature of the intermediate in eq 3 is not our concern here; rather, we wish to compare how well the k–T data fit eq 2 with the fit for a combination of eq 4–6, namely,

$$k_{obsd} = \exp(A/T + B)/[1 + \exp(C/T + D)] \quad (7)$$

Equation 7 requires a nonlinear regression of the k–T data, and the algorithm reported by Wentworth[6] provides a suitable tool for such an enterprise. The same algorithm can be used for eq 2, although traditionally this calculation has been accomplished by a linear least-squares technique. Since the Wentworth regression is weighted, minor differences related to eq 2 are apparent between the nonlinear and linear calculations, but these are not significant in the present context. Since the Valentiner and Albery–Robinson fits require three and four parameters, respectively, the Gauss criterion for goodness of fit (Ω)

$$\Omega = [\Sigma\delta^2/(n - p)]^{1/2} \quad (8)$$

is used to assess the relative merits of eq 7 and 2 where $\delta = k_{obsd} - k_{calcd}$, n = number of (k–T) pairs, with $p = 3$ (A, B, and C) for the Valentiner equation and $p = 4$ (A, B, C, and D) for the Albery–Robinson expression.

The data in Tables I and II show the Albery–Robinson equation to be distinctly superior for both substrates. It is of interest to note that the Albery–Robinson equation gives rise to two numerical fits (see Table III). These are mathematically equivalent but chemically different when A, B, C, and D are given physical significance (see also Moore[7]).

The present results lend further support to our previous conclusions based on an alternative treatment of the k–T data for ethyl bromide and *sec*-propyl methanesulfonate.[4] Again we emphasize that the Albery–Robinson approach assumes real $\Delta C_p^{\ddagger}$ terms to be absent in relation to the k_1 and α quantities. This assumption is probably incorrect, but modification of eq 5 and 6 to accomodate real heat capacity terms would require a six-parameter nonlinear fit. Since the residuals relating the four-parameter nonlinear fits are already small (see Tables I and II) and are less than the sum of the estimated errors on the experimental k values, it appears pointless to include real $\Delta C_p^{\ddagger}$ terms in eq 5 and 6. Thus the present results are indicative rather than definitive as to the existence of intermediates in these reactions. The evidence presented here should nevertheless prove useful in future mechanistic discussions related to these and numerous other displacement reactions which demonstrate a similar non-Arrhenius temperature dependence.

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(6) J. E. Wentworth, *J. Chem. Educ.*, **42**, 96 (1965).

(7) W. S. Dorn and D. D. McCracken, Numerical Methods with Fortran IV Case Studies, Wiley, New York, 1977 p 351.

(8) N. W. Alcock, D. J. Benton, and P. Moore, *Trans. Faraday Soc.*, **66**, 2210 (1970).

Neutral Products from Nucleophilic Substitution in the Gas Phase. Displacement of Water from Protonated Secondary Alcohols[1]

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Many textbooks present second-order nucleophilic substitution as a reaction that exemplifies the use of stereochemical studies to infer transition-state geometry. Inversion of configuration occurs not only in solution but also for anionic S_N2 reactions (displacement of Br^- by Cl^- on a neutral molecule) in the gas phase.[2] Recently, Speranza and Angelini[3] have described γ-radiolysis studies that suggest backside displacement also predominates in a cationic S_N2 reaction in the gas phase (displacement of HCl by H_2O on protonated methylchlorocyclohexanes). These latter results show only a 2:1 ratio of diastereomers, however, and were run under conditions (e.g., reactants at atmospheric pressure) where the effects of competing pathways and reactions on surfaces are not controlled.

$$ROH + ROH_2^+ \xrightarrow{-H_2O} R_2OH^+ \quad (1)$$

$$R_2OH^+ \xrightarrow{NX_3} R_2O \quad (2)$$

We wish to report the stereochemistry of a cationic S_N2 displacement on a protonated alcohol (reaction 1) under conditions where the effects of competing pathways may be assessed. Over

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(1) Portions of this work were presented at the 28th annual meeting of the American Society for Mass Spectrometry, New York, May 26, 1980.

(2) Lieder, C. A.; Brauman, J. I. *J. Am. Chem. Soc.* **1974**, *96*, 4029–4030.

(3) Speranza, M.; Angelini, G. *J. Am. Chem. Soc.* **1980**, *102*, 3115–3120.

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